

REMARKS

Claims 3-5, 14 and 15 have been canceled. Claims 1, 2, 6-13, 16-18 and 27 and new Claim 28 are active in the case. Reconsideration is respectfully requested.

The present invention relates to a process for the upgrading of hydrocarbon mixtures that boil within the naphtha range and which contain sulfur impurities.

Claim Amendment

Claim 1 has been amended in order to limit the catalytically active metals of the catalyst to a combination of molybdenum and cobalt, as disclosed in Example 1, for instance. The limitation of Claim 1 to a combination of cobalt and molybdenum and the specification of the HDS/HYD ratio in the claim has necessitated the cancellation of Claims 3-5 and amendments to Claims 6-8. The claim has also been amended to make a minor grammatical correction thereto.

New Claim 28 has been presented which is similar to active Claim 1, but which in addition specifies an HDS/HYD ratio, as shown in several of the tables in the specification, which is at least a value of 1.9 which is shown in Table 4 (first row). Entry of the amendments to the claims and new Claim 28 is respectfully requested.

Invention

As claimed, the present invention is a process of hydrodesulfurizing a hydrocarbon mixture, by reacting a hydrocarbon mixture containing olefins and having a boiling range

within the range of C₄ to 250° C, and a sulfur content of at least 150 ppm with hydrogen in the presence of a catalytic composition comprising:

a) an acidic carrier consisting of a silica and alumina gel, amorphous to X-rays, with a molar ratio SiO₂/Al₂O₃ of 30/1 to 500/1, having a surface area ranging from 500 to 1000 m²/g, a porosity of 0.3 to 0.6 ml/g and a pore diameter within the range of 10-40 Å; and

b) a mixture of molybdenum and cobalt deposited on the carrier in an overall quantity ranging from 2 to 67 % by weight with respect to the total amount of components (a) + (b), thereby effecting said hydrodesulfurization with concomitant skeletal isomerization of the olefins of said mixture under the hydrogenation conditions of the process which results in a ratio HYD/ISO ranging from 0.7 to 2.5, wherein HYD is the ratio of non-isomerized olefins that have been hydrogenated to olefins in the hydrocarbon mixture and ISO is the ratio of isomerized, hydrogenated and non-hydrogenated olefins to the sum of isomerized, hydrogenated and non-hydrogenated olefins and non-isomerized hydrogenated and non-hydrogenated olefins.

Applicants emphasize that the hydrocarbon mixture is one which boils within the stated range and is a mixture of both paraffinic hydrocarbons and olefins. In fact, a preferred embodiment of the hydrocarbon mixture is a full range naphtha having a boiling range of 35° -250° C. As a result of contacting the hydrocarbon mixture with hydrogen in the presence of the catalyst as defined in the claims, not only is significant hydrodesulfurization of the mixture obtained, but also importantly, from the viewpoint of obtaining a hydrocarbon product that exhibits a high octane rating, the olefin component of the hydrocarbon undergoes significant isomerization with minimal hydrogenation of the olefins to paraffinic material.

Prior Art Rejection

Claims 1-18 and 27 stand rejected based on 35 USC 103(a) as obvious over Hart U.S. Patent 3,156,640 in view of Bellussi et al EP-340868. This ground of rejection is respectfully traversed.

The Examiner indicates in his comments on page 3 of the Office Action that Hart discloses a process for the simultaneous isomerization of olefins and hydrodesulfurization of a hydrocarbon mixture that has a boiling point within the gasoline or naphtha range. While this statement is correct insofar as the statement is presented, it is, very importantly, incomplete. What is missing is that, as stated in lines 14-19 of column 1, not only are olefins in the feed material used isomerized, but the isomerization of the olefins is **accompanied by the extensive hydrogenation of the olefins** to isoparaffin product. This desired and achieved objective is clearly shown in the example of the patent in columns 5 and 6 where a feed mixture of 120 ml of a light cracked fraction and 380 ml of sulfur-containing naphtha is hydrogenated over a catalyst with the result that a fraction was produced which was not only extensively hydrogenated, as indicated by a bromine number < 1 , but also was a product in which the olefins were extensively isomerized while being hydrogenated to isoparaffins, thereby producing a product of high octane numbers.

The present process stands in material distinction from the process of Hart, because, while the present process achieves the extensive hydrogenation and removal of sulfur impurities from the hydrocarbon feed employed and extensive isomerization of olefins in the feed, nevertheless, a **markedly reduced hydrogenation of the olefins is achieved** while the olefins are isomerized. It is this feature of the present process that patentably distinguishes the

present process as claimed from the reference. This very desirable feature is achieved **only with** a specific acidic catalyst, which is the silica/alumina gel as defined in subparagraph (a) of present claim 1, which catalyst is neither shown nor suggested by Hart.

The effectiveness of the present process is shown in examples of the present process, and, in particular, two Examples, i.e., 11 and 12, that are comparative. Examples 8 to 10 of the application describe catalyst embodiments of the present invention in hydrogenation reactions. Tables 2 to 4 of the text demonstrate the very superior ability of the catalyst system of the invention in promoting **selective isomerization** of olefins in the reacting starting material **as opposed to significant hydrogenation of the isomerized olefin material** to saturated product by virtue of the comparatively very low "HYD/ISO" ratios found in the three tables. On the other hand, for the comparative catalyst Catalyst F of Example 11, which is a combination of molybdenum and cobalt supported on γ -alumina in a commercially available catalyst and is thereby within the scope of catalysts shown in Hart, the columns ISO %, HYD % and HYD/ISO show a low content of isomerized unsaturates accompanied by extensive reduction of olefinic material to saturated hydrocarbons (high HYD/ISO ratio). A very similar situation is shown in Example 12 of the reference which is based on catalyst G which is a known Co/Mo catalyst in which the support is acid silica/alumina gel. Very high HYD/ISO ratios are shown which indicate very significant hydrogenation of olefin in comparison to non-hydrogenated, isomerized olefin. Accordingly, it is clear that the recitation of the ratio HYD/ISO of 0.7 to 2.5 in the present claims is important in defining the present invention over the prior art.

As to the matter of catalyst composition, while the broad disclosure of the Hart patent includes the possibility of combining cobalt and molybdenum in a supported catalyst,

nevertheless, the example of the patent only describes a catalyst based on nickel as the catalytically active metal. Thus, the catalyst of the reference does not have to be a combination of cobalt and molybdenum. Moreover, the silica/alumina support of the catalyst of the example at 13 % by wt alumina and 87 % by wt silica has a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 11.3, whereas the present claims require a catalyst support in which the $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio ranges from 30/1 to 500/1.

It also should be noted that amended Claim 1 of the invention is distinguished over the Hart patent on the basis of the hydrogenation conditions of the present process. On the other hand, the patent describes hydrogenation at 100 to 500° C and at 60 atm (in the example). No WHSV is disclosed in the patent and there is no teaching of the 200 to 400 times as much hydrogen as the quantity of hydrocarbons present in the reaction. Clearly, the Hart patent does not teach or suggest the present invention as claimed.

As to newly presented Claim 28, the arguments for patentability advanced above apply as well to Claim 28. In addition, another significant limitation in the present claims is the HDS/HYD ratio which is specified as being at least 1.9. This ratio for the product of any given reaction is that of the extent of desulfurization conversion (HDS) to hydrogenation activity (HYD) which is the ratio of non-isomerized olefins that have been hydrogenated to olefins in the hydrocarbon mixture. As shown in Tables 2-4 for experiments within the scope of the invention, HDS/HYD ratios are obtained of a value of at least 1.9 which values show high conversions to desulfurized product versus minimum hydrogenation of olefins in the hydrodesulfurization reaction of the present invention. The comparative examples of the specification in Tables 5-7 show lower HDS/HYD ratios on the order of about 1, although one

experiment in Table 5 shows a HDS/HYD ratio of 2.4. These data certainly indicate a greater extent of hydrogenation of olefins activity than is desired in the present invention.

Applicants submit that the deficiencies of Hart are neither overcome nor improved upon by Bellussi et al. It is clear that the silica/alumina material disclosed in Bellussi et al is the same material which is used as the support for the catalytically active Group VIII and VIB metals used to prepare the catalyst system of the present invention which achieves the hydrodesulfurization results of the present invention. However, it should be noted that the publication at the top of page 4 describes the utility of the silica-alumina gel of the reference in only four types of reactions which are the dimerization of olefins, the isomerization of olefins, the alkylation of hydrocarbons with olefins and the dewaxing of hydrocarbon material. Hydrogenation of olefins is **not** disclosed. Thus, if the silica-alumina gel of the reference is used in an olefin isomerization reaction, the gel, without added metal, achieves the isomerization reaction. This is a teaching that obviously is inconsistent with the present invention, but also the Hart patent where the catalyst comprises a suitably reactive metal supported on an acid carrier material. In the only exemplified reaction of the reference, the reaction shown in Example 10 is the totally unrelated reaction (to Hart as well as the present invention) of the dimerization of: (i) a mixture of linear isomers of tetradecene, (ii) 7-tetradecene or (iii) 1-octene. None of these hydrocarbon materials is the unsaturated feedstock of the present process, as well as the feedstock of the process of Hart.

The Examiner had asserted that because the Hart patent teaches a catalyst in which catalytically active metal is supported on an acidic silica/alumina catalyst, one of skill in the art would be led to substitute the silica/alumina gel of Bellussi et al for the known silica/alumina

support materials shown in Hart to arrive at the present invention. However, applicants submit to the contrary that, because of the lower acidity of the acidic silica/alumina gel catalyst of Bellussi et al, one of skill in the art would expect that upon substitution of the silica/alumina gel catalyst of Bellussi et al for the silica/alumina supports disclosed by Hart, the resulting catalyst, when used in the process of Hart would, in the presence of hydrogen, exhibit **both less isomerization and hydrogenation** of olefins. The finding of the present invention, to the contrary, is that by using a catalyst in which Groups VIB and VIII metals are supported on the silica/alumina gel catalyst material of Bellussi et al, it is possible to **desulfurize** a mixture of hydrocarbons that contains olefins and sulfur, and at the same time achieve very significant skeletal isomerization of the olefin component of the hydrocarbon starting material of the present process **without** effecting significant hydrogenation of the olefins. (This effectively refutes the Examiner's comment that the "modified process of Hart would have the HYD/ISO ratio as presently claimed.) Accordingly, applicants submit that the present invention is not obvious in view of the teachings of the combined references, and withdrawal of the rejection is respectfully requested.

Appl. No. 10/777,225

Reply to the Office Action of April 8, 2005

It is believed that the application is in proper condition for consideration for allowance.

Early notice to this effect is earnestly solicited.

Respectfully submitted,

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Norman F. Oblon

A handwritten signature in black ink, appearing to read "FD Vastine". The signature is fluid and cursive, with the first letters of the first and last names being capitalized and prominent.

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